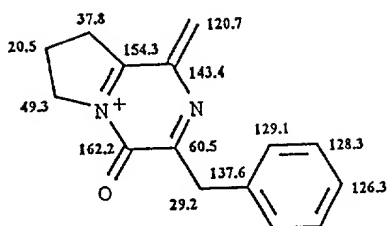
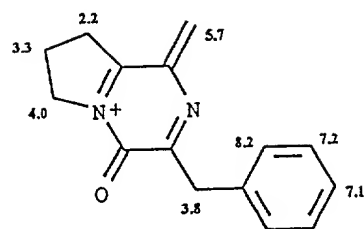


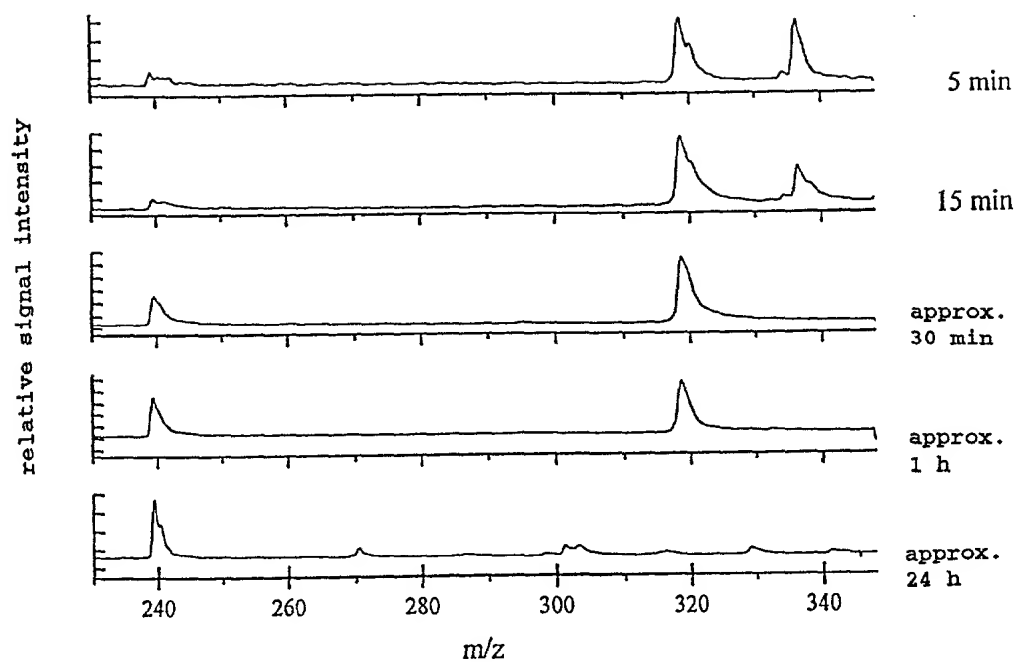
$^{13}\text{C}$  NMR data



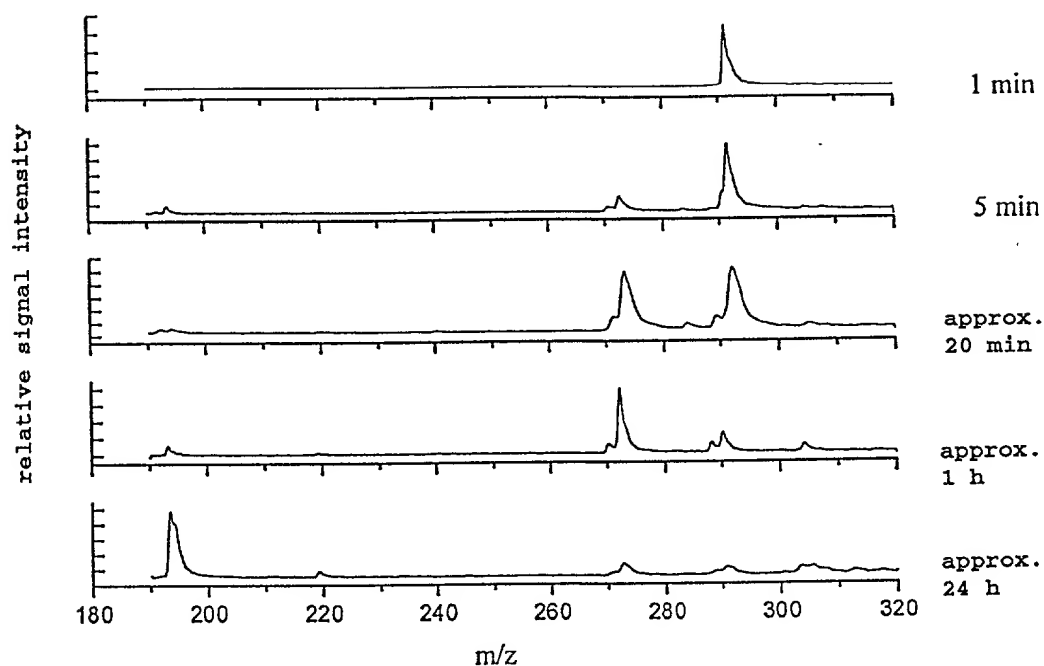
$^1\text{H}$  NMR data



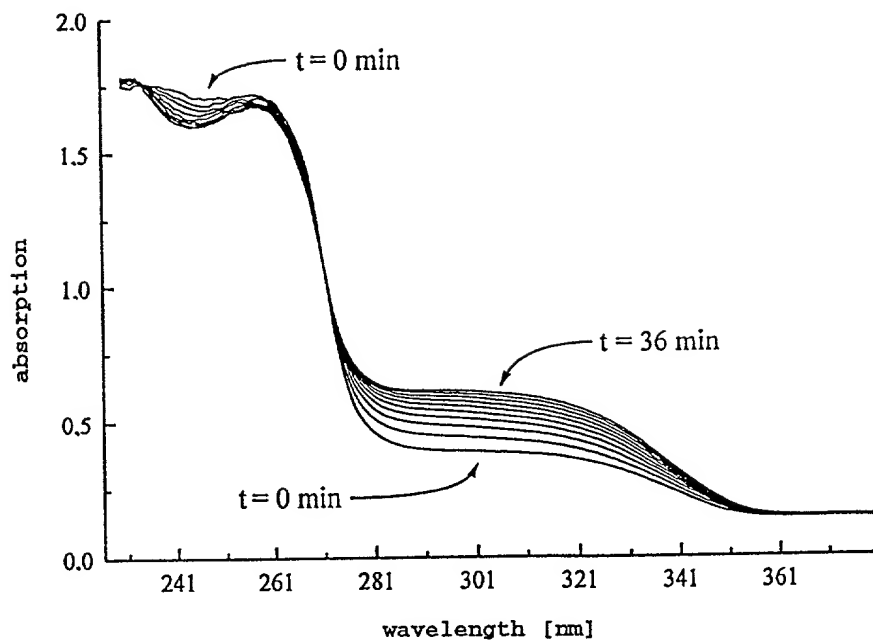
**Figure 1:** Structural formula of the product of the intramolecular cyclisation of H-Phe-Pro-pyridinium methyl ketone. The characteristic chemical displacements (in ppm) determined by means of  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR are assigned to the corresponding atoms.



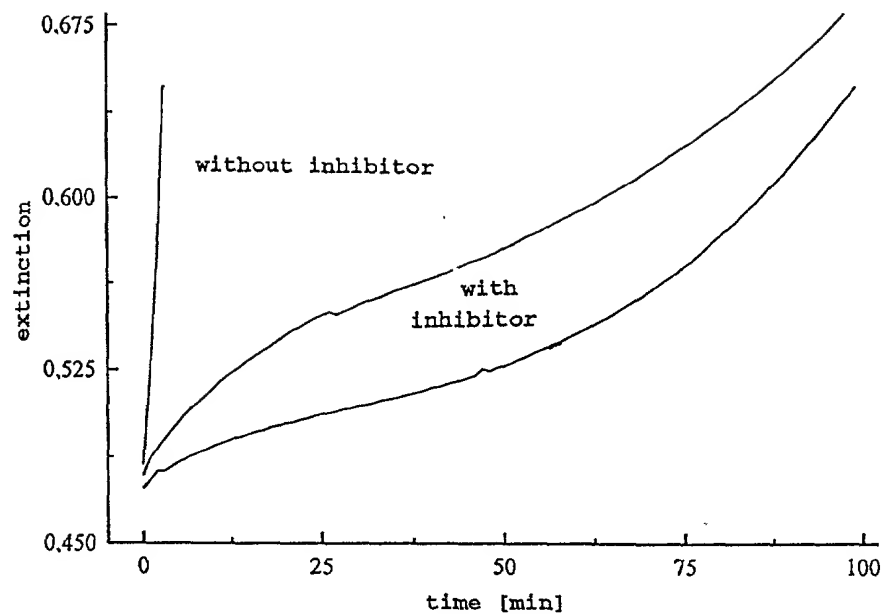
**Figure 2:** MALDI-TOF mass spectra of the cyclisation of H-Phe-Pro-pyridinium methyl ketone in an aqueous buffer solution pH = 7.6, recorded according to the incubation period.



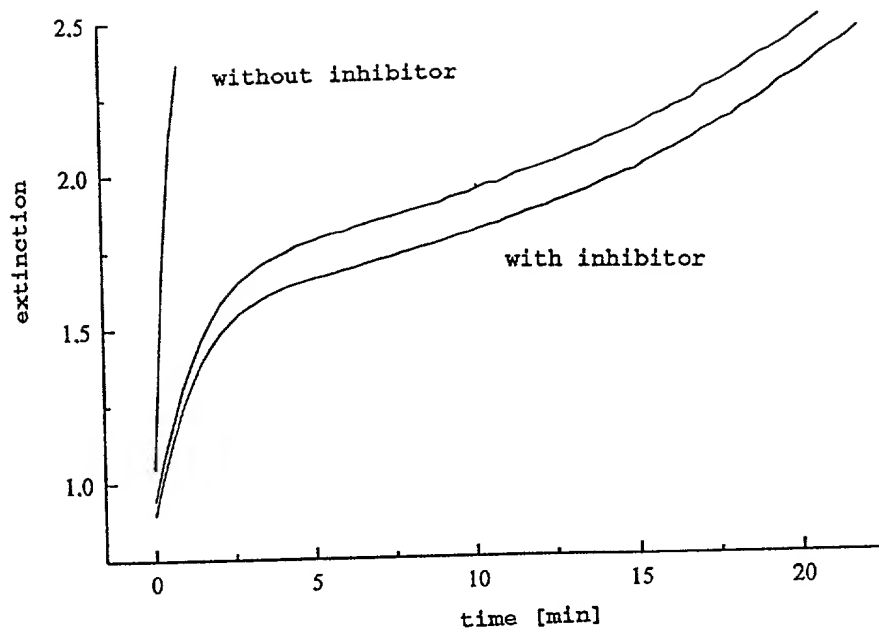
**Figure 3:** MALDI-TOF mass spectra of the cyclisation of H-Val-Pro-pyridinium methyl ketone in an aqueous buffer solution pH = 7.6, recorded according to the incubation period.



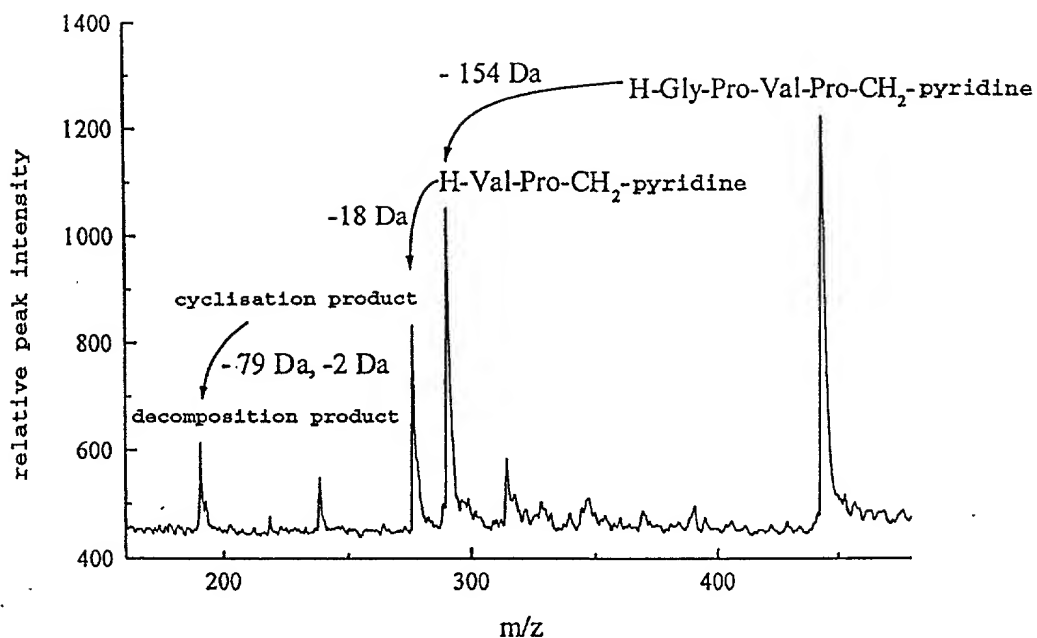
**Figure 4:** UV spectra of an aqueous solution of H-Phe-Pro-pyridinium methyl ketone incubated in 0.1M HEPES buffer, pH = 7.6, at 30°C. The cyclisation reaction was monitored over a period of 40 minutes.



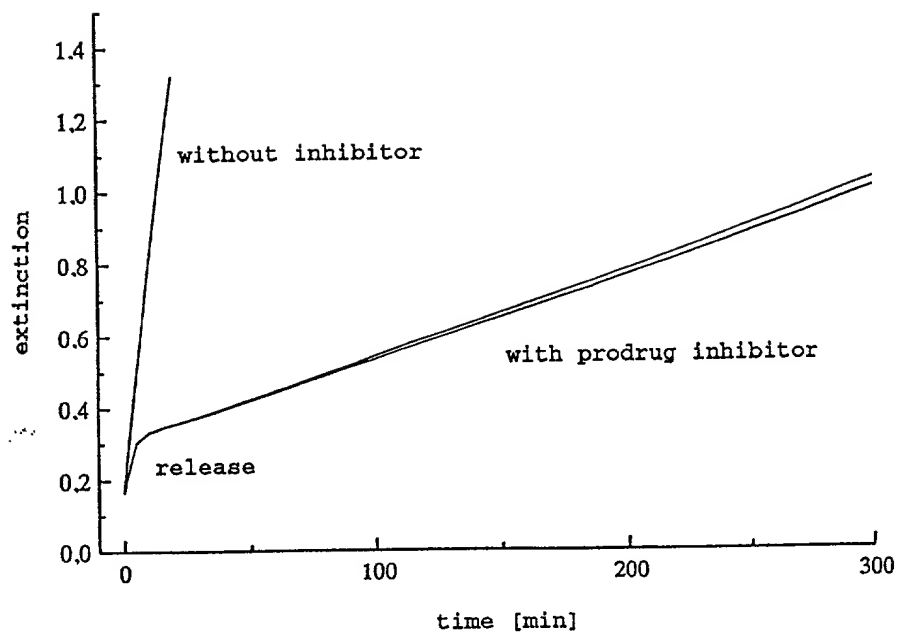
**Figure 5:** Progress curves of the DP IV-catalysed hydrolysis of the substrate H-Gly-Pro-pNA in the presence of  $2.8 \times 10^{-3} \text{ M}$  H-Val-Pro-pyridinium methyl ketone,  $0.06 \text{ } \mu\text{g/ml}$  of DP IV,  $4 \times 10^{-4} \text{ M}$  H-Gly-Pro-pNA in the batch,  $0.1 \text{ M}$  HEPES buffer,  $\text{pH} = 7.6$ ,  $30^\circ\text{C}$ .



**Figure 6:** Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of  $2.1 \times 10^{-4} \text{ M}$  H-Phe-Pro-pyridinium methyl ketone,  $0.06 \text{ } \mu\text{g/ml}$  of DP IV,  $1.0 \times 10^{-3} \text{ mol/litre}$  of H-Gly-Pro-pNA in the batch,  $0.1 \text{ M}$  HEPES buffer,  $\text{pH} = 7.6$ ,  $30^\circ\text{C}$ .



**Figure 7:** MALDI-TOF mass spectrum of the incubation batch of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of  $2.6 \times 10^{-5}$  mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06  $\mu\text{g/ml}$  of DP IV,  $2.0 \times 10^{-4}$  mol/litre of H-Gly-Pro-pNA, 0.1M HEPES buffer, pH = 7.6, 30°C. Recorded after an incubation period of 60 minutes.



**Figure 8:** Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-pNA in the presence of  $2.6 \times 10^{-5}$  mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06  $\mu\text{g/ml}$  of DP IV,  $2.0 \times 10^{-4}$  mol/litre of H-Gly-Pro-pNA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.